

BAKAYAN, H.T.

Mechanism of the reaction of formation of 2,5-dimethyl-3-hexyne-2,5-diol. A. T. Bakayan. *J. Gen. Chem.* (U.S.S.R.) 8, 628 (in French 607) (1938); cf. C. A. 32, 7894. According to Kazarian (C. A. 20, 39789), the reaction of condensation of KOH and CaC_2 with Me_2CO in Et_2O proceeds by the intermediate formation of $\text{KC}(\text{C}(\text{CaOH}))_2$, which combines with 1 and 2 mols. Me_2CO . Subsequent hydrolysis with H_2O produces 3-methyl-2-butyn-1-ol (I) and 2,5-dimethyl-2,5-hy-

droxy-3-hexyne (II), resp. B. disputes the above reaction scheme and suggests that II is formed by the interaction of the intermediate compd. of K and Me_2CO with CaC_2 and not with C_2H_2 formed in the hydrolysis: $\text{Me}_2\text{CO} + \text{KOH} \rightarrow \text{Me}_2\text{C}(\text{OH})\text{OK}$ (III); $2\text{III} + \text{CaC}_2 \rightarrow (\text{KOCMe}_2)_2\text{C}(\text{C}_2\text{H}) + \text{Ca}(\text{OH})_2$. The decompn. of the alcoholate with H_2O gives free II. This reaction scheme is supported by the following evidence. Conducting CO_2 into the reaction mixt. to bind the KOH and to prevent the reaction of C_2H_2 with Me_2CO before the hydrolysis gave equal yields of II. It follows that KOH is the active agent in that phase of the reaction when only CaC_2 and not free C_2H_2 is available. The decompn. of the gelatinous reaction mixt. with CO_2 and subsequent distn. showed no presence of C_2H_2 group, giving ROH and Me_2CO in the proportions corresponding to III. The latter is capable of reacting with CaC_2 in Et_2O , producing the alcoholate, which with H_2O gives II. To prove that I is not directly produced in the condensation of Me_2CO with KOH and CaC_2 , the reaction mixt. was filtered, the residue was freed from any by-products by washing with dry Et_2O and then decompd. with acidulated H_2O at 0° , giving II and no other products. The presence of traces of I in the filtrate (before the hydrolysis) indicates that it is contained in the reaction mixt. not in the form of $\text{KOCMe}_2\text{C}(\text{C}_2\text{H})\text{CaOH}$, as claimed by Kazarian, but as the sol. free I. Its absence in the filter residue shows that it is formed as a result of the secondary reaction of partial alk. decompu. of II.

Chas. Blanc

ASH-55A METALLURGICAL LITERATURE CLASSIFICATION

10

CA

BARAYAN, A.T.

PROCESSES AND PROPERTIES

The splitting of acetylene γ -glycols by the action of potassium carbonate. A. T. Barayan, *J. Gen. Chem.* (U. S. S. R.) 9, 306-400(1939).—When compds. of the type $R_2C(OH)C\equiv CC(OH)R$, are heated with K_2CO_3 , they either split to give 1 mol. of ketone and the corresponding unsatd. alc. (reaction 1), or 2 mols. of ketone and C_2H_2 (reaction 2), depending on the electronegativity of the R groups. 3,6-Dimethyl-4-octyne-3,6-diol (I) splits 95% by reaction (1) and 5% by reaction (2). 1,2-Dicyclohexylacetylene splits 85% by (1) and 15% by (2). 2,5-Dimethyl-3-hexyne-2,5-diol (II) splits 80% by (1) and 20% by (2). 2,6-Diphenyl-3-hexyne-2,5-diol splits 30% by (1) and 70% by (2), and 1,1,4,4-tetraphenyl-2-butyne-1,4-diol splits 100% by (2). Only compds. in which R is aliphatic form phenylurethans. The phenylurethan of I m. 201-2°, that of II m. 200°. 3-Methyl-1-butyne-3-ol and $PhNCO$ give $(PhNH)_2CO$. H. M. Leicester

COMMON ELEMENTS

ASB-514 METALLURGICAL LITERATURE CLASSIFICATION

ISSUED MAY 1957

RECEIVED MAY 1957

ENERGY, n. 7.2

CH

Catalytic action of *p*-toluenesulfonic acid on acetylene glycols. 1. The action on 2,5-dimethyl-3-hexyne-2,5-diol and 3,6-dimethyl-4-octyne-3,6-diol. A. Hattayan, *J. Gen. Chem. (U. S. S. R.)* **9**, 1410-11 (1959). Preliminary results showed that acetylene glycols react with *p*-McCl₃·SO₃H (I) by cleaving 2 mols. H₂O and forming corresponding divinylacetylenes. Thus, the distn of 4.9 g. 2,5-dimethyl-3-hexyne-2,5-diol with 0.07 g. I at 140°C. gave 91.1% divinylacetylene, b. 11-20°, by 35% under similar conditions 3,6-dimethyl-4-octyne-3,6-diol, 0.14 g. and 0.08 g. I yielded 90% 1,7,7,6-tetramethyl-3-octadiene, b. 160°.

Chas. Blanc

Chas. H. H. H.

A 34.32.4 METALLURGICAL LITERATURE CLASSIFICATION

1304: 174-88, 174

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COMMON ELEMENTS		PROCESS AND PROPERTIES INDEX		COMMON VARIABLES INDEX	
BARAJAN, A. T. BC		2-3		ASB-SLA METALLURGICAL LITERATURE CLASSIFICATION	
Reaction of cyclohexanone glycols. A. BARAJAN, S. AMIRJAN, and H. J. KIRKMAN (J. Gen. Chem. Russ., 1959, 31, 2222-2223). C₆H₁₀ is passed into Et₂O-OMe solution containing KOH, at 9-10° (1-3 hr.). The mixture is cooled, after 24 hr., and the Et₂O layer is separated and distilled; the residue consists chiefly of (OMe-OMe-OMe), OOMeEt similarly affords (OMe-OMe-OMe), and cyclohexanone gives di-(2-hydroxyethyl)acetylene. R. T.		FROM DIVISION		FROM DIVISION	
SECTION 111 DIV 111		SECTION 111 DIV 111		SECTION 111 DIV 111	

BAKHYAT R. T.
1A

The synthesis of unsymmetrical acetylenic γ -glycols
A. Babayan, *J. Gen. Chem.* (U. S. S. R.) 10, 497 2
(1940); cf. *C. A.* 34, 2780. When ketones react with
 C_2H_2 in the presence of KOH, they give compds. of the
structure $R_2C(OH)C\equiv CH$. If, instead of isolating this
compd., the mixt. is treated with an equimol. amt. of
another ketone and the mixt. is cooled and stirred, further
reaction takes place to give $R_2C(OH)C\equiv C(OH)R'$.
MeqCO and C_2H_2 mixts. thus treated with MePhCO give
2,5-dimethyl-3-heptyne-2,5-diol, b. 213-10°, d₄²⁰ 0.9170,
n_D²⁰ 1.400, MR 45.81. When the 2nd ketone is MePhCO,
2,5-dimethyl-3-octyne-2,5-diol, b. 222-7°, d₄²⁰ 0.9321,
n_D²⁰ 1.4568, MR 49.64, is obtained, and when cyclohexa-
none is used, the product is unsym-dimethylpentamethylene-
are at least as effective as Ac_2O in polysulfone formation.
 H_2O_2 , Br_2O_3 or lauroyl peroxide was ineffective when used
in place of H_2 ; mineral acids could not be replaced by Ac_2O .

Chem. Inst. Armenian Affil., AS USSR

AND SLA DETAILING LITERATURE CLASSIFICATION

10

CHENYAN, H.T.

ea

The synthesis of unsymmetrical acetylene glycols
 H. A. T. Chenyan, *J. Gen. Chem. (U. S. S. R.)* 10,
 1177-82 (1940); cf. *C. A.* 34, 7851^a.--The method pre-
 viously used is modified by prep. and purifying methyl-
 butynol, and treating this with various ketones and KOH
 in abs. Et₂O. By thus running the process in 2 steps,
 purer final products are obtained. In this way are prepd.
 91% yields of 2,5-dimethyl-3-heptyne-2,5-diol, m. 44-5°;
 92% 2,5-dimethyl-3-octyne-2,5-diol, b.p. 225-8°, 97% di-
 methylpentamethylenebutynediol (Me₂C(OH)C≡C(OH)
 (CH₂)₅CH₂), m. 94-5°, 78% 2-methyl-3-ethyl-3-heptyne-
 2,5-diol, m. 39-40°, 90% 1-isopropyl-2-6-methyl-3-o-
 hexylolacetylene (Me₂C(OH)C≡C(OH)CH₂CH₂CHMe-
 CH₂CH₂), b.p. 130-1°, 90% 2,3-dimethyl-1-undecyne-2,5-
 diol, b.p. 170-2°, 15% 2-methyl-3-phenyl-3-hexyne-2,5-diol,
 m. 81°, 40% 1,1-dimethyl-4,4-diphenyl-3-butyne-1,4-diol
 (I), m. 114-15°. The sym. isomer of I, m. 158-62°, is
 obtained in 20% yield from MePhCO, KOH and C₆H₆
 in Et₂O. Similarly, Ph₂CO, KOH and C₆H₆ give 83%
 tetraphenylbutynediol, m. 192°. These last syntheses
 show that the reaction cannot go entirely through the
 formation of enols. H. M. Leicester

ASS. SLA METALLURGICAL LITERATURE CLASSIFICATION

DATE: 11/11/50

RECORD: 11/11/50

REVISION: 11/11/50

11/11/50

SYNTHESIS AND DEGRADATION OF ACETYLENIC γ-ESTERS. A. Balayan (Chem. Inst., Brevan). *Bull. Armenian Branch Acad. Sci. U.S.S.R.* 1941, No. 5/6 (10/11), 121-45 (in Russian); cf. *C.A.* 34, 7831⁹; 35, 2858⁹.—A satisfactory method for the prepn. of acetylenic glycols with 70-80% yields was developed. KOH (60 g.), 150 cc. Et₂O, and 20 g. Me₂CO were treated with stirring at 13-15° with 5 l. dry C₂H₄ over 40 min.; after standing for 2.5 hrs. the mixt. was hydrolyzed, and the org. layer was neutralized with CO₂ and distd. to yield 76.5% 2,5-dimethyl-3-hexyne-2,5-diol, b.p. 105-200°, m. 94°; slow distn. of this in the presence of p-MeC₆H₄SO₂ gave 80% bis(1-methylvinyl)acetylene, b. 123-4°, n_D²⁰ 1.4848, d₄²⁰ 0.7863. KOH (28 g.), 100 cc. Et₂O, 10 g. Me₂CO, and 4 l. C₂H₄ gave analogously 64.6% 3,6-dimethyl-4-octyne-3,6-diol, b. 215-20°, m. 64-6°, and a small amt. of 3-methyl-1-penten-3-ol, b. 115-40°; the diol dehydrated as above gave 83.0% 3,6-dimethyl-2,5-octadien-4-yne, b. 167-71°, n_D²⁰ 1.4901, d₄²⁰ 0.8002. Similarly, 20 g. KOH, 100 cc. Et₂O, and 9 g. Me₂CO gave with C₂H₄ (65°) 3,6-diethyl-4-octyne-3,6-diol, b. 215-8°, m. 78°, and a small amt. of 3-ethyl-1-penten-3-ol, b. 128-50°; the diol on dehydration as above gave 65.3% of the corresponding diethyloctadienyne, b. 107-9°, n_D²⁰ 1.4920, d₄²⁰ 0.8007. Me hexyl ketone gave 65% 7,10-dimethyl-5-hexadecyne-7,10-diol, m. 80°; cyclohexanone gave 73.0% bis(1-hydroxycyclohexyl)acetylene, m. 110°, which on dehydration as above gave 80% dicyclohexenylacetylene, b. 175-80°, n_D²⁰ 1.537, d₄²⁰ 0.9057. 2-Methylcyclohexanone gave (81°) bis(6-methyl-2-hydroxycyclohexyl)acetylene, m. 122°, and a small amt. of (6-methyl-2-hydroxycyclohexyl)acetylene, b.p. 80 (10)°, m. 65-6°; 3-methylcyclohexanone gave bis(3-methyl-1-hydroxycyclohexyl)acetylene, 72°, m. 103-6°, while 4-hydroxycyclohexylacetylene gave 70% bis(4-methyl-2-hydroxycyclohexyl)acetylene, m. 150°; acetophenone gave 50% 2,5-diphenyl-3-hexyne-2,5-diol, m. 158-62°, while p-MeC₆H₄CO₂Me gave 45% 2,5-di-p-tolyl-3-hexyne-2,5-diol, m. 120° (from MeOH). Ph₂CO gave, in a 4-day reaction with C₂H₄ (82°), tetraphenylbutynediol, m. 102° (from CHCl₃). KOH (30 g.), 100 cc. Et₂O, and 10 g. Me₂CO were treated with ice cooling with 10 g. 3-methyl-3-butyn-2-ol in 50 cc. Et₂O; after standing for 3 days the mixt. was hydrolyzed and worked up as above to give 91% 2,5-dimethyl-3-heptyne-2,5-diol, m. 44-5°, b. 210-12°, n_D²⁰ 1.452, d₄²⁰ 0.8026; dehydration of this as above gave 78% 2,5-dimethyl-1,5-heptadien-3-yne, b. 141-7°, n_D²⁰ 1.4880, d₄²⁰ 0.79658; Me₂PrCO in the above reaction gave 2,5-dimethyl-3-octyne-2,5-diol, b.p. 225-8°, while Et₂CO gave 67.5% 2-methyl-5-ethyl-3-heptyne-2,5-diol, b.p. 220-4°, m. 10°, which gave on dehydration 80% 2-methyl-5-ethyl-2,5-heptadien-3-yne, b. 158-61°, n_D²⁰ 1.4878, d₄²⁰ 0.7987; Me hexyl ketone gave 60% 2,5-dimethyl-3-hendecyne-2,5-diol, b.p. 170-2°, KOH (13.5 g.), 60 cc. Et₂O, and 0 g. Me₂CO gave, with 6 g. 3-methyl-1-penten-3-ol, 65% 3-methyl-6-ethyl-4-octyne-3,6-diol, b. 230-4°, m. 60° (from light petr.), which on dehydration as above gave 92.0% 3-methyl-6-ethyl-2,5-octadien-4-yne, b. 176-83°, n_D²⁰ 1.4939, d₄²⁰ 0.8072. KOH (30 g.), 100 cc. Et₂O, 11 g. cyclohexanone, and 10.8 g. 2-methyl-3-

BABAYAN, A.T.; TERZYAN, A.G.

Synthesis of β -dialkylaminobutanones. Dokl. AN Arm. SSR 9 no.3:
105-110 '48. (MIRA 9:10)

1. Khimicheskiy Insitut Akademii nauk Armyanskoy SSR, Yerevan.
Predstavleno G.Kh. Bunyatyanom.
(Butanone)

Babayan, A. T.

Synthesis of lepidine and its analogs with substituents in the aromatic ring. A. T. Babayan and N. P. Gumbaryan. *Sbornik Stat-1 Obshch. Khim. Akad. Nauk S.S.S.R.* 1: 688-714 (1953); cf. C.A. 47, 3266f. — Some 70-80% yields of lepidine and its homologs are obtained by cyclization of α -(o-aminoaryl)butanones in the presence of HCl, ZnCl₂, and FeCl₃. Heating 22.5 g. FeCl₃, 8.2 g. 4-phenylamino-2-butanone, 1.1 g. ZnCl₂, 5 ml. 35% HCl, and 60 ml. EtOH 6 hrs. on a steam bath, followed by evapn. and addn. of NaOH gave 81.5% lepidine; picrate, m. 211-12°. Similarly 4-(o-tolylamino)-2-butanone gave 72% 4,8-dimethylpicric acid (picrate, m. 216-18°); 4-(p-tolylamino)-2-butanone gave 82% 6-methyllepidine (picrate, m. 236-37°); 1-(p-aminophenyl)-2-butanone gave 82.8% 6-methylelepidine (picrate, m. 221-22°). Heating 36.2 g. N-(γ -chlorocrotyl)amine, 20 g. KOH, and 50 ml. iso-AmOH 4 hrs. at reflux gave 67.6% 1-phenylamino-2-butanone, b_p 112-113°, d₂₀ 1.0167, n_D²⁰ 1.5739; this (14.5 g.), 6.3 g. PhNO₂, 7 ml. H₂SO₄, 1 g. H₂O, and 30 ml. MeOH refluxed 8 hrs. gave 40.1% lepidine, probably formed through intermediate formation of 4-phenylamino-2-butanone. Heating 193.4 g. (MeCCl₂CHCH₂)₂NMe₂Cl and 114.4 g. 1-C₆H₅NH₂ 7 hrs. at 130-140° gave 86% dimethylchlorobutenylamine and 90% N-(γ -chlorocrotyl)-1-naphthylamine (I), b_p 199-201°, d₄ 1.1591, n_D²⁰ 1.6535. Similar reaction with 2-C₆H₅NH₂ gave 90% N-(γ -chlorocrotyl)-2-naphthylamine (II), b_p 200-2°, d₄ 1.1485, n_D²⁰ 1.6512. I (29.3 g.) treated with cooling with 10 ml. concd. H₂SO₄, evolved HCl, after standing for a considerable time (unstated) the mixt. was neutralized and extd. with Et₂O, yielding 21.7% 7,8-benzolelepidine, isolated as picrate, m. 216-17°. Similarly II gave 41.4% 5,6-benzolelepidine (picrate, m. 221-22°; free base, m. 100-1°. Free 7,8-isomer, m. 77-8° (cf. Visbeck, C.A. 44, 3995b). G. M. Kosolapoff

USSR.

Synthesis of 4,7-dimethylquinoline. A. T. Babayan and Nina P. Gambaryan. *Izv. Akad. Nauk SSSR, Ser. Fiz.-Mat. Nauk* 1953, No. 2, 78-8; *Refer. Zhur. Khim.* 1954, No. 12718. — Hydrolysis of *N*-(γ -chlorocrotyl)-*m*-toluidine (I) in the presence of H_2SO_4 yields 4,7-dimethylquinoline (II). It is assumed that the reaction proceeds through an intermediate stage at which 4-(*m*-tolylamino)-2-butanone (III) is formed, but does not sep. since, in carrying out the reaction under conditions which prevent the formation of III, II cannot be obtained. On cyclization there apparently also forms 4,7-dimethyl-1,2,3,4-tetrahydroquinoline; its presence is proved by the fact that oxidation of the mixt. obtained during cyclization doubles the yield of II. Dehydrochlorination of I forms *N*-(β -butynyl)-*m*-toluidine (IV) which upon hydration forms II. A mixt. of 77.0 g. dimethylbis(γ -chlorocrotyl)ammonium chloride (V) and 64.2 g. *m*-toluidine (VI) is heated for 10 hrs. 130-40°, a soln. of 25 g. of KOH added, and the org. layer distd., giving 1. b.p. 123-8.5°, n_D^{20} 1.5502, d_4^{20} 1.0507; yield based on V 73, 1/2

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and based on VI, 90%. To 61.6 g. of VI and 31.9 g. of 1,3-dichloro-2-butene is added 25 g. of H₂O and the upper layer is distilled, yielding 66% I. To 12.1 g. of I is added with cooling 40 ml. H₂O, the mixt. is stirred 12 days, neutralized with Na₂CO₃, extd. with ether, and the ether evapd., giving 11 g. substance (VII) from which was sep'd. II (picrate, m. 227° (from Na₂CO₃), yield 16.9%, mp 267° (from nitrobenzene). Crude material (0.93 g.) obtained in hydrolysis of VII was heated on a water bath with 0.15 g. ZnCl₂, 1.25 g. FeCl₃, 0.5 g. concd. HCl, and 11 ml. alc. The mixt. is alkalized and steam distilled, giving II. Treating I in the same way yields only 1% II. To 13.5 g. 1.1 g. KOH, and 15 ml. abs. alc. were heated 12 hrs. on a water bath, after which it was dil'd. with H₂O, extd. with ether, and distilled to obtain 68% IV, bp 152°/0.5 mm. (d. 1.062). A mixt. of 1.4 g. IV, 0.54 g. concd. H₂SO₄, 0.2 g. HgO, and 8 ml. MeOH, heated to boil on a steam bath, the alc. driven off, and the residue extd. with ether, yields 44.8% II picrate. M. Hosh

BABAYAN, A. T.

CZECH

Transformations of semicarbazones of β -substituted ketones. I. Semicarbazones of β -arylamino ketones. A. Babayan and N. P. Gamberyan. Zhurnal Obshchei Khimii, 1965, 35, 1245-1247, 10 refs.

"APPROVED FOR RELEASE: 06/06/2000

CIA-RDP86-00513R000102810013-5

semicarbazone is very low (2-3%).

G. M. ~~_____~~

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BABAYAN, A. T.

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The mechanism of cyclization of β -arylamino-butanones
A. T. Babayan and N. P. Gombaryan. *Izvest. Akad. Nauk
Armen. S.S.R., Ser. Fiz.-Mat. i Tekhn. Nauk* 6, No.
5/6, 99-100 (1953) (in Russian; Armenian summary); cf.
C.A. 47, 3206f. — Using 1-amino-3-butanone (I) as an ex-
ample, it was shown that the main part of the β -arylamino-
butanones (II) decomps. upon heating with HCl, FeCl₃, and
ZnCl₂ to the aromatic amine and methyl vinyl ketone before
cyclization occurs. This shows that the cyclization of I re-
sulting in the formation of lepidine is similar to the Skraup
and Dobner-Müller reaction. It was established that the
quinoline bases can be prepd. by the reaction of an aromatic
amine with compds. which can split out methyl vinyl ketone,
e.g., I and its N-Me and N-Ac derivs. 5,6-Benzolepidine was
prepd. in 91.4% yield by the reaction of β -naphthylamine
with I. J. Boytar Leach

Chem. Inst. as Arme.SSR

① AA JFW

BABAYAN, A. T.

USSR. ~~Realkylation reaction. I. A. T. Babayan, N. P. Gam-~~
~~baryan, and N. N. Ganybaryan, Doklady Akad. Nauk~~
~~Arm. S.S.R. 17, No. 2, 30-44 (1953) (in Russian; Armen-~~
~~ian summary, 45).~~ 3-Chloro-2-butenylamines of better
purity are prepd. in higher yield when (MeCCl:CHCH₂)₂
NMe₂Cl (I) rather than 1,3-dichloro-2-butene (II) is used as
an alkylating agent. It is shown that: (1) alkylation of
amines with I takes place without intermediary formation
of II; (2) tertiary amines are realkylated, when treated with
I, exchanging their Me group for the chlorobutenyl radical;
(3) realkylation is easily accomplished using (MeCCl:CH-
CH₂)₂NMe₂OH instead of I; (4) MeCCl:CHCH₂NMe₂·HCl
(III) is more difficult to realkylate than the amine itself; (5)
when I is heated at 170-80° for a long time the chlorobutenyl
radical splits off and chloroprene resins, III, and HCl salts
of Me₂N and MeN(CH₂CH:CClMe)₂ are formed. CH₃N-
(Me)CH₂CH:CClMe, b_p 128-30, is prepd. in 97.4% yield
by heating equimolar amts. of I and PhNMe₂ for 16 hrs. at
155-60°. (MeCCl:CHCH₂)₂NMe₂, b_p 115-10, is prepd.
similarly in 95.5% yield from III free base. Cf. Snyder, et
al., C.A. 44, 9929f.

Chem. Inst., Arm. Acad. Sci -

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[illegible]

BABAYAN, A.T.; MKRYAN, G.M.; VARTANYAN, N.G.

~~Isomerization~~ Isomerization of 1-dialkyl aminobutenes-2. Dokl. AN Arm. SSR 19 no.3:
83-84 '54. (MIRA 8:7)

1. Predstavleno A.L. Mndishoyanom. (Butene)

BABAYAN, A.T.

E-2

USSR/Organic Chemistry. Synthetic Organic Chemistry.

Abs Jour: Ref Zhur-Khimiya, No 6, 1957, 19037.

Author : Babayan A. T., Gambayan N.

Inst :

Title : Alkylation in an Aqueous Medium in the Presence of Quaternary Ammonium Salts.

Orig Pub: Zh. Obshch. Khimiyi, 1954, 24, No 10, 1887-1893.

Abstract: The alkylation reactions of acetoacetic ester (I), acetylacetone (II), malonic ester (III) by the action of 1,3-dichlorobutene (IV), $\text{CH}_2=\text{CHCH}_2\text{Cl}$ (V) and $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ (VI) in an aqueous-alkaline media in the presence of catalysts $(\text{CH}_3)_2\text{NCH}_2\text{CH}=\text{CClCH}_3$ (VII) are described. By the interaction of I with IV, I with V, and I with VI in the presence of VII (1:1 : 0.1) in an aqueous solution of KOH by heating, is obtained $\text{CH}_3\text{COCHRCOOC}_2\text{H}_5$ (VIII) (enumerated are R, yield in %, b.p. in °C/mm):

Card : 1/5

USSR/Organic Chemistry. Synthetic Organic Chemistry.

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Abs Jour: Ref Zhur-Khimiya, No 6, 1957, 19037

action proceeds because of the presence of the haloid alkyl, and that the alkyls of the quaternary ammonium salt in the conditions described does not participate in the reaction. Attempts of alkylating fluorene and naphthalene by heating them with XI in an anhydrous medium did not give the expected results. The interaction of 0.1 mole $C_6H_5C=CH$ with 0.1 mole XI by heating (14 hours 160-165°) gave a mixture of substances, from which was isolated 7.4 g. of a compound boiling at 163-164°/14 mm, apparently tri-(3-chlorobutenyl)-phenylacetylene. At the reaction I with XI and III with XI in analogous conditions is obtained IX, yield 37%, and X, yield 22.6%.

Card : 3/3

BAK/AN. A.T.

USSR/Organic Chemistry, Synthetic Organic Chemistry.

E-2

Abs Jour: Ref Zhur-khimiya No 6, 1957, 19126

Author : Babayan A. T., Grigoryan A.A.

Inst : ~~USSR Academy of Sciences~~

Title : Alkylation in an Aqueous Medium in the Presence of
Quarternary Ammonium Salts. II. Nitrogen-alkylation
of Aromatic Amines.

Orig Pub: Izv. AN ArmSSR, ser. Fiz-Matem. Yestiestv. and Tekhn.
N., 1955, 8, No 4, 81-88

Abstract: N-alkylation of aromatic amines $ArNH_2$ (I), 1,3-dichlorobutene-2 (II), and $C_6H_5CH_2Cl$ with the formation of $ArNHR$ ($R = 3\text{-chlorobutenyl}$ (III), $R = C_6H_5CH_2$ (IV)) in an aqueous-alkaline medium ($NaOH$ or Na_2CO_3) proceeds with a higher yield (~ 2 times) in the presence of a catalyst - quarternary ammonium salts, than in the absence of the latter at the same duration of the reaction. The yield in the absence of the catalyst

Card : 1/3

USSR/Organic Chemistry. Synthetic Organic Chemistry.

E-2

Abs Jour: Ref Zhur-khimiya No 6, 1957, 19126.

remains low even on the prolongation of the reaction time 2-3 times. To 0.2 mole I, Ar-C₆H₅ (Ia), 0.02 mole of dimethyl-di-(3-chlorobutenyl)-ammonium chloride (V) in 10 cc water and 0.2 mole II is added during 20 minutes 15.3 g. KOH in 30 cc water (heated to 45-48°), stirred 5 minutes more, III was obtained (Ar=C₆H₅), yield 54%, b.p. 123-128°/2 mm, n_D²⁰ 1.5731, d₄²⁰ 1.1056. in an analogous manner (at 50-60°, 30-50 min.) are obtained the following III (given Ar, yield in percent, b. p. in °C/mm, n_D²⁰, d₄²⁰): 2-CH₃C₆H₄ 64.5 (61.8 with Na₂CO₃), 133-137/4, 1.5661, 1.0857; 2-CH₃C₆H₄, 60, 140-145/2, 1.5716, 1.1395; 3-CH₃OC₆H₄, 60, 170-175/5, 1.5645, 1.1410; 4-CH₃OC₆H₄, 73.2, 153-156/12, 1.5663, 1.5663, 1.1403; 4-C₂H₅OC₆H₄, 69.2, 175-180/5, 1.5566, 1.118; α-Naphthyl (at 85-90°), 80.7, 178-180/2, 1.6387, 1.1533; β-Naphthyl (at 75-80°), 73, 185-190/2, 1.6457,

Card : 2/3

BABAYAN, A. T.

6

Cleavage of quaternary ammonium bases. I. Syn-
thesis of mixed tertiary amines. A. T. Babayan, N. G.
Vartanyan, and I. Ya. Zurbayev (Zurbaev, Inst. Krivan).
Zhur. Obshchei Khim. 25, 1610-13 (1955).—To 25 g. (CH_2 :
 CMeCH_2)₂(MeCCl:CHCH_2)₂NHBr heated on a steam bath
 was added 14 g. NaOH in 50 ml. H_2O , resulting in distn. of
 7.8 g. liquid and 1.5 l. gaseous product; the latter forms an
 explosive Ag salt (vinylacetylene and chloroprene mixt.),
 while the liquid was mainly chloroprene. The acidic soln.
 treated with NaOH gave (CH_2 : CHCH_2)₂NH, b_{p} 58-60°;
 picrate, m. 112°. Thus, 78 g. $\text{Me}(\text{PhCH}_2)(\text{MeCCl:CH-}$
 $\text{CH}_2)\text{NCl}$ and aq. NaOH gave vinylacetylene, chloroprene,
 and 22 g. $\text{Me}_2\text{NCH}_2\text{Ph}$, b_{p} 170-2° (picrate, m. 91.5-5°).
 $\text{MeEt}(\text{MeCCl:CHCH}_2)_2\text{NBr}$ similarly gave 77.4% MeEt-
 $(\text{MeC:CCH}_2)_2\text{N}$, b_{p} 133-5°, n_D^{20} 1.4397, d_4^{20} 0.8165, and 5.8
 g. $\text{MeEt}(\text{MeCCl:CHCH}_2)_2\text{N}$, b_{p} 152-5°, n_D^{20} 1.4529, d_4^{20}
 0.9316. $\text{Me}(\text{PhCH}_2)(\text{MeCCl:CHCH}_2)_2\text{NCl}$ gave 61% Me-
 $(\text{PhCH}_2)\text{NCH}_2\text{C:CMc}$, b_{p} 115-16°, d_4^{20} 0.951, n_D^{20} 1.521,
 and a lesser yield of $\text{C}_{10}\text{H}_{10}\text{N}$, b_{p} 138-60° (crude), b_{p} 138-40°,
 d_4^{20} 0.99074, n_D^{20} 1.5553, which is either $\text{MeN}(\text{CH}_2\text{C:CMc})$ -
 $(\text{CHPhCH}_2\text{C:CMc})$ or $\text{MeN}(\text{CH}_2\text{C:CMc})[\text{CH}(\text{CH}_2\text{Ph})\text{C:CMc}]$.
 $\text{MeEt}(\text{PhCH}_2)(\text{MeC:CCH}_2)_2\text{NBr}$ similarly gave
 $\text{MeEt}(\text{PhCH}_2)_2\text{N}$, b_{p} 100-51, b_{p} 187-90°, d_4^{20} 0.9215, n_D^{20}
 1.5068 (picrate, m. 113.5-14.5°). G. M. Kosolapoff

CH
NO'S.

M. 951

②

Quaternary ammonium salts IV. Decomposition of
trialkylsulfonium salts A. F. Babayan, G. M.

410 A mixture of the salts was heated in a 100°C oil bath. The residue was dried in a vacuum oven at 100°C for 24 hours.

on a water bath, filtered, the water distilled, the residue dried and then reprecipitated from the oil bath. Yield 75% (calculated for 100% conversion).

Chem. Inst. AS Acad. SSR

"APPROVED FOR RELEASE: 06/06/2000

CIA-RDP86-00513R000102810013-5

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APPROVED FOR RELEASE: 06/06/2000

CIA-RDP86-00513R000102810013-5"

BABAYAN, A. T.

E-2

USSR/Organic Chemistry, Synthetic Organic Chemistry.

Abs Jour: Ref Zhur-Khimiya No 6, 1957, 19075

Author : Babayan A.T., Grigoryan A.A.,

Inst :

Title : Investigation in the Series of Quarternary Ammonium Compounds II. The Formation of Tetrolic Acid at the Interaction of Iodic Trimethyl-(2,2,3,3-tetrachlorbutyl)-ammonium with an Aqueous Alkali.

Orig Pub: Zh. Obshch. Khimiyi, 1956, 26, No 7, 1945-1948.

Abstract: By the chlorination of dimethylaminobutene-2(I) 1-dimethylamino-2,2,3,3-tetrachlorobutane (II) is obtained. At the interaction of iodomethylate II (III) with an alkali, a complete dehydrochlorination of II with the formation of trimethylamine (IV) and tetrolic acid (V) takes place. In a solution 242.5 g. of I in 350 cc of a 34% HCl (acid) is passed 430 g. Cl₂, alkalized with K₂CO₃, extracted with ether, II is

Card : 1/3

INDZHIKYAN, M.G.; SURMANYAN, S.A.; BABAYAN, A.T.

Investigations in the field of quaternary ammonium compounds.
Report No.8: Stability of bonds of certain organic radicals in
quaternary ammonium compounds. Izv. AN Arm. SSR Ser. khim. nauk
10 no.3:213-221 '57. (MIRA 10:12)

1. Khimicheskiy institut AN ArmSSR.
(Ammonium compounds) (Chemical bonds)

INDZHIKYAN, M.G.; BABAYAN, A.T.

Quaternary ammonium compounds. Report No.4: Stevens rearrangement
of ammonium compounds. Izv. AN Arm. SSR ser. khim. nauk 10 no.6:
411-419 '57. (MIRA 11:6)

1. Khimicheskiy institut AN ArmSSR.
(Ammonium compounds) (Rearrangements (Chemistry))

COUNTRY : USSR
 CATEGORY : Pharmacology, Toxicology. Different Preparations
 LIT. SOUR. : Zhurnal., No. 121958, No. 56760
 AUTHOR : Babayan, A.T.
 TITLE : The Pharmacological Action and Toxicity of Dimethyl-butylene-amine, dimethyl-(3-chlorocrotyl)-amine, and methyl-di-(3-chlorocrotyl)-amine.
 PERIOD. PUB. : Farmakol. i Toksikologiya, 1957, Vol.20, No.1, 74-42
 SUMMARY : Studies were made of the toxicity of dimethyl-butylene-amine (I), dimethyl-(3-chlorocrotyl)-amine (II), and methyl-di-(3-chlorocrotyl)-amine (III) in rabbits and mice following administration intravenously, subcutaneously, by inhalation, cutaneously, and perorally. By all routes of administration, the action of the preparations was uniform. At first there was restlessness (abrupt movements, strong respirations, dilatation of the pupils), replaced by suppression with weakened reactions to sound, light, and painful stimuli, weakening of respirations, and of cardiac activity, reduction in blood pres-
 Card: 1/3

COUNTRY :
CATEGOR : ✓

REF. NO. : RB101, No. 1958, No.

AUTHOR :
INST. :
TITLE :

REF. NO. :

ABSTRACT : sure, diminution of the secretory and motor functions of the stomach. Upon intravenous injection in rabbits, death occurred in not less than two-thirds of the animals during the course of 10-40 minutes at doses for I of 1.2 gm, for II of 0.8 gm, and for III of 0.4 gm. Saturation of the solution of III at 20 degrees led to death of 100% of the animals within 3 days upon daily administration; saturated solution of II caused death in 100% when given daily for seven days; and saturated solution of I caused 80% death rate when given for a period of ten days. With application to the skin, all

COUNTRY :
CATEGORY :
ABS. JOUR. : ZhBiol., No. 1256, No.
AUTHOR :
ISS. :
TITLE :

ABSTRACT :

: substances caused inflammation, accompanied by necrosis of the surface layers. Minimum lethal doses, upon application to the skin in the pure form, were 12 gm for I, 8 gm for II, and 4 gm for III. I was active against avian tubercle bacilli and ixodid ticks. III against enteric bacilli, and II against streptococcus and staphylococcus. -- N.I. Zelyakova

"APPROVED FOR RELEASE: 06/06/2000

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APPROVED FOR RELEASE: 06/06/2000

CIA-RDP86-00513R000102810013-5"

BABAYAN, A.T.; KROMYAN, T.V.

Third joint session of the chemical institute of the Academies of
Sciences of three Transcaucasian republics. Izv.AN Arm.SSR.
Khim.nauki 11 no.2:135-137 '58. (MIRA 11:11)
(Chemistry--Congresses)

BABAYAN, A.T.; MOZGOV, I.Ye.; GRIGORYAN, A.A., akademik; KASHEIN, M.G.

Synthesis and pharmacological tests of some amines and ammonium salts containing polyhalide radicals. Dokl. AN Arm. SSR 26 no.2: 81-93 '58. (MIRA 11:5)

1.Chlen-korrespondent AN Armyanskoy SSR (for Mozgov). 2.Vsesoyuznaya akademiya sel'skokhozyaystvennykh nauk im. V.I. Lenina (for Grigoryan). 3.Khimicheskiy institut Akademii nauk Armyanskoy SSR i Moskovskaya veterinarnaya akademiya.
(Amines) (Ammonium salts) (Halides)

BABAYAN, A.T.; GRIGORYAN, A.A.; MARTIROSYAN, G.T.

Splitting of quaternary ammonium salts containing alkyl halides
by an alkali hydroxide. Dokl. AN Arm. SSR 26 no.3:153-162 '58.
(MIRA 12:10)

1. Chlen-korrespondent AN Argyanskoy SSR (for Grigoryan).
(Sodium hydroxide) (Ammonium salts)

BABAYAN, A.T.; INDZHIKYAN, M.G.; SURMANYAN, S.A.

Comparative stability of bonds between the allyl and benzyl radicals and nitrogen. Dokl AN Arm. SSR 26 no.4:235-240 '58.
(MIRA 11:5)

- 1.Chlen-korrespondent AN Armyanskoy SSR (for Indzhikyan).
- 2.Institut organicheskoy khimii Akademii nauk Armyanskoy SSR.

(Allyl) (Benzyl) (Nitrogen)

AUTHORS: Babayan, A. T., Mkryan, G. M., 79-28-5-30/69
Gyuli - Kevkhyan, R. S.

TITLE: Investigations in the Field of Amines and
 Quaternary Ammonium Compounds (Issledovaniya v oblasti
 aminov i chetvertichnykh ammoniyevykh soedineniy)
 X. Synthesis of Isoprene of α , β - and γ , γ' -
 -Dimethylallylchlorides (Polusheniye izoprena iz α , β - i
 γ , γ' -dimetilallilkhloridov)

PERIODICAL: Zhurnal Obshchey Khimii, 1958, Vol. 28, Nr 5,
 pp. 1259-1263 (USSR)

ABSTRACT: The present report deals with the synthesis by alkaline
 cleavage of the quaternary ammonium salts obtained by
 conversion of the α , β - and γ , γ' -dimethylallylchlorides
 with tertiary amines (see scheme 1). For the latter were
 used: dimethylisocamyl-, dimethyl(γ , γ' -dimethylallyl)-,
 -dimethylbenzyl- and dimethyl-(butine-2-yl)-amines. The
 conversion of the compound (III) with amines takes place
 very energetically. The chlorine (IV) reacts slowly and
 demands heating. The alkaline cleavage of the obtained

Card 1/3

Investigations in the Field of Amines and
Quaternary Ammonium Compounds

79-28-5-30/69

X. Synthesis of isoprene of α, β - and γ, δ -
-Dimethylallylchlorides

quaternary ammonium salts, from the salts with the radical butine-2-yl, lead to the formation of isoprene in a yield of 58 - 85%, and of the corresponding tertiary amine (67 - 89 %). The alkaline cleavage of the quaternary ammonium salts obtained by conversion of the mentioned chlorides with 1 - dimethylaminobutanol - 2, resulted in the formation of vinylacetylene and the corresponding tertiary amine (see scheme 2). These results speak in favor of a easy movability of the radical butine-2-yl and correspond to the earlier obtained data on the cleavage of the quaternary ammonium salts with this radical, dimethyl- γ, δ -dimethylallylamine also forms by alkaline cleavage of the quaternary ammonium salt which is obtained by conversion of the γ, δ dimethylallylchloride with dimethylamine dissolved in water. According to the data of references (reference 6) it can be expected that the chloride (V) in the conversion with tertiary amine does not form the compound (V) but the

Card 2/3

Investigations in the Field of Amines and
Quaternary Ammonium Compounds

79-28-5-30/69

X. Synthesis of Isoprene of α , β - and γ , δ -
-Dimethylallylchlorides

compound isomeric to it (VI) or a mixture of both
(see scheme 3). The structure of the synthesized
salts has not been explained hitherto. The results of
the alkaline cleavage of the synthesized quaternary
ammonium salts are mentioned in a table. There are
1 table and 6 references, 4 of which are Soviet.

ASSOCIATION: Institut khimii Akademii nauk Armyanskoy SSR
(Institute for Chemistry, AS Armenian SSR)

SUBMITTED: May 3, 1957

Card 3/3

5(4), 5(3)

AUTHORS:

Babayan, A. T., Indzhikyan, M. G., Neyman, E. B.

SOV/62-59-1-33/38

TITLE:

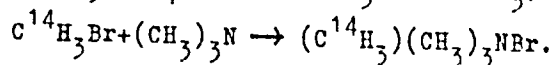
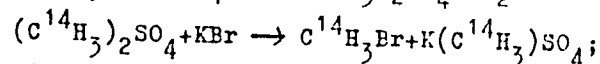
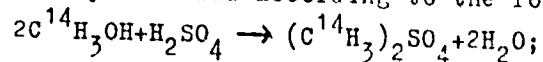
On the Equivalence of Nitrogen Bonds in Tetramethyl-Ammonium Bromide (O ravnotsennosti svyazey azota v bromistom tetrametilammonii)

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 1, pp 174 - 174 (USSR)

ABSTRACT:

According to modern concepts the 4 nitrogen bonds in $(CH_3)_4NBr$ formed by sp^3 bastardization are equivalent. In the present paper the authors checked these data. $(C^{14}H_3)(CH_3)_3NBr$ was synthesized according to the following scheme:



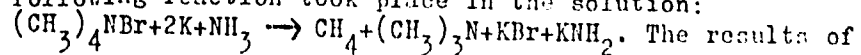
Card 1/2

The last process took place at -80° . Furthermore, the product obtained was decomposed in liquid ammonia solution. The

On the Equivalence of Nitrogen Bonds in Tetramethyl-
Ammonium Bromide

SOV/62-59-1-33/36

following reaction took place in the solution:



The results of the investigation are summarized in the table. It may be seen from it that methane separated during the decomposition of the ternary salt possesses 23% of the activity, whereas trimethyl amine possesses 78%. Thus, the experiments carried out at -80° confirmed the conclusions of the paper (Ref 1) and the generally assumed idea of the equivalence of the bonds of quadrivalent nitrogen. There are 1 table and 2 references, 1 of which is Soviet.

ASSOCIATION:

Institut khimicheskoy fiziki Akademii nauk SSSR (Institute of Chemical Physics of the Academy of Sciences, USSR)

SUBMITTED:

Institut organicheskoy khimii Akademii nauk ArmSSR (Institute of Organic Chemistry of the Academy of Sciences, Armenian S.R.)
June 20, 1958

Card 2/2

5(1,3)

AUTHOR:

Babayan, A. T.

SCV/153-2-4-24/32

TITLE:

Synthesis of Monomers Via Chlorine Derivatives

PERIODICAL:

Izvestiya vysshikh uchebnykh zavedeniy. Khimiya i khimicheskaya tekhnologiya, 1959, Vol 2, Nr 4, pp 594 - 600 (USSR)

ABSTRACT:

A report on this paper was given at the All-Union Conference on "Ways of Synthesis of Initial Products for the Production of High Polymers" which took place in Yaroslavl from September 29 to October 2, 1958. Quaternary ammonium salts containing a 3-chlorobutene-2-yl-radical are easily separated into tertiary amine as well as a mixture of chloroprene and vinyl acetylene under the effect of aqueous alkali. The presence of the latter indicates that the radical mentioned is partly dehydrated before the ammonium complex is separated (see Diagram). In order to extend the above dehydrochlorination reaction, the author dealt with the preparation of various tertiary amines containing chlorine, the iodine methylates of which were separated by means of aqueous alkali. Most amines were prepared from 1,3-dichlorobutene-2 according to diagram 1. Moreover, amines were obtained from 1,2,4-trichlorobutene-2 and chlorobutenes of the allyl type

Card 1/ 3

Synthesis of Monomers Via Chlorine Derivatives

SCV/153-2-4-24/32

as well as from chloroisoamylenes. The reaction mentioned takes place already at room temperature, does not stand temperatures higher than that of a boiling water bath, and rarely takes place at 115-120°. Table 1 shows the separation results (products without nitrogen only). The yield of trimethyl amine was almost equal to the theoretical yield. On account of this example and additional ones, the mutuality of the dehydrochlorination reaction, i.e. of the separation of quaternary ammonium salts containing a halogen in the radical, was proved: this reaction can be successfully used in the synthesis of compounds with conjugated double bonds. The reaction mentioned is of theoretical as well as practical importance because it is simple, easy to carry out, and the products prepared are of high purity. Chlorobutenes and chloroisoamylenes of the allyl type are easily dehydrochlorinated into butadiene (yield 85-90%) and isoprene (yield 60-85%), respectively, by means of aqueous alkali in the presence of catalytical amine quantities (see Diagram). As was to be expected, unsaturated compounds could be obtained in the thermal separation of amines (Table 2). For these reasons, investigations of diene synthesis on the basis of petroleum isopentane were started. These investigations were carried out together with the

Card 2/3

Synthesis of Monomers Via Chlorine Derivatives

SOV/153-2-4-24/32

Yerevanskiy zavod imeni Kirova (Yerevan Works imeni Kirov) in its central laboratories. It was more suitable, however, to start from isoamylenes. The author worked out a preparation diagram of isoprene and β -chloroisoprene from trimethyl ethylene (see Diagram). A new copolymer rubber was obtained by means of copolymerization of β -chloroisoprene with chloroprene. It has less tendency towards crystallization as compared with mass-produced nairite but the rest of its properties do not differ from those of the latter. This β -chloroisoprene is superior to other monomers because its polymerization rate is close to that of chloroprene. The ratio of members in the copolymer obtained is equal to that in the initial charge. Difficulties appear in the further dehydration of isoamylenes to isoprene as well as in ridding the latter from impurities. There are 1 scheme, 2 tables, and 2 Soviet references.

ASSOCIATION: Institut organicheskoy khimii AN ArmSSR (Institute of Organic Chemistry of the Academy of Sciences, Armyanskaya SSR)

Card 3/3

BABAYAN, A.T.; MKRYAN, G.M.; GRIGORYAN, A.A.;

Cleavage of quaternary ammonium salts. Trudy Inst.khim.AN
Azerb.SSR 17:131-137 '59. (MIRA 13:4)
(Ammonium salts)

BABAYAN, A.T.; INDZHIKYAN, M.G.

Alkylation in an aqueous medium in the presence of quaternary ammonium salts. Dokl. AN Arm. SSR 28 no.2:67-71 '59.
(MIRA 12:6)

1. Institut organicheskoy khimii AN ArmSSR. 2. Chlen-korrespondent AN ArmSSR (for Babayan).
(Ammonium salts) (Alkylation)

SOV/79-29-2-8/71

AUTHORS: Babayan, A. T., Grigoryan, A. A., Martirosyan, G. T.

TITLE: Investigations in the Field of Amines and Ammonium Compounds (Issledovaniya v oblasti aminov i ammoniyevykh soyedineniy). XI. On the Problem of the Influence of Nitrogen and the Molecular Structure Upon the Stability of the Bonds in the Amines and Quaternary Ammonium Compounds, With an Alkyl Halide (XI. K voprosu vliyaniya kharaktera azota i stroeniya molekuly na prochnost' svyazey v aminakh i chetvertichnykh ammoniyevykh soyedineniyakh, soderzhashchikh galoidalkil)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 2, pp 386-398 (USSR)

ABSTRACT: As already earlier (Ref 1) reported, the authors investigated the influence of the nitrogen nature and the molecular structure upon the bond stability in the above-mentioned nitrogen compounds containing an alkyl halide. For the purpose of a wider application of the dehydrochlorination cleavage (Ref 2) of the quaternary ammonium salts in the synthesis of compounds with conjugate double bonds, the authors extended their investigation also to tertiary and quaternary ammonium salts, with alkyl polyhalides. The following compounds were synthesized here:

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SOV/79-29-2-8/71

Investigations in the Field of Amines and Ammonium Compounds. XI. On the Problem of the Influence of Nitrogen and the Molecular Structure Upon the Stability of the Bonds in the Amines and Quaternary Ammonium Compounds, With an Alkyl Halide

1-dimethyl-amino-3-chloro butane (V)-3-chloro butene-3(VII),-3,4-dichloro butene-3(VIII),-2,3,3-trichloro butane (X),-3,3,4-trichloro butane (XI),-3,3,4,4-tetrachloro butane (XII),-3,4,4-trichloro butene-3(XIII). In addition, the reaction of these amines was carried out with alcoholic alkali lye as well as the alkaline cleavage of the iodine methylates: (Va), (VIa), (VIIIa), (Xa), (XIa), and (XIIa). Dimethyl-amino butene-2(I) (Scheme 1) served as initial product. Hydrochlorination took place through a flow of dry HCl through molten hydrochloric salt of the amine at 140-160°. The results of hydrochlorination agree with expectations (Table 1, Nr 1-3). The chlorination of the aqueous solutions of the amines designated in the scheme proceeds smoothly and yields products, in which chlorine adds to the double bond. The chlorination results are given in table 1 (Nr 4-7). The hydrochlorination of the monosubstituted dialkyl-amino acetylene agrees with Markovnikov's rule, whereas that of the disubstituted one, under the influence of the ammonium group leads to the

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SOV/79-29-2-6/71

Investigations in the Field of Amines and Ammonium Compounds. XI. On the Problem of the Influence of Nitrogen and the Molecular Structure Upon the Stability of the Bonds in the Amines and Quaternary Ammonium Compounds. With an Alkyl Halide

affiliation of chlorine to the carbon atom, which is the farthest from nitrogen. The results proved the general validity of dehydrochlorination cleavage with aqueous alkali lye of quaternary ammonium salts containing alkyl halide and its applicability in the synthesis of compounds with conjugate double bonds. Proof was also found of the rules governing the cleavage rate of hydrogen chloride in dependence on the character on nitrogen and on the structure of the alkyl halides connected with it. There are 4 tables and 17 references, 10 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii Akademii nauk Armyanskoy SSR (Institute of Organic Chemistry of the Academy of Sciences, Armyanskaya SSR)

SUBMITTED: December '6, 1957
Card 3/3

BABAYAN, A.T.; MARTIROSYAN, G.T.

Thermal splitting of ammonium salts containing a β,γ -unsaturated radical. Dokl. AN Arm. SSR 30 no.5:271-277 '60. (MIRA 13:8)

1. Institut organicheskoy khimii Akademii nauk Armyanskoy SSR.
2. Chlen-korrespondent AN Armyanskoy SSR (for Babayan).
(Ammonium salts)

S/020/60/133/006/027/031XX
B016/B054

AUTHORS: ~~Babayan, A. T.~~ Indzhikyan, M. G., and Bagdasaryan, G. B.

TITLE: Formation of Conjugate Diene Amines During the Interaction of Mono- and Diquaternary Salts of 1,4-Diamines With Aqueous Alkali

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol. 133, No. 6, pp. 1334-1336

TEXT: The authors report on their investigations of the reactions of mono- and diquaternary salts of 1,4-di-(dimethyl-amino)-2-methyl butene-2. They attempted to find out whether the double 1,4-cleavage of the di-ammonium salt takes place simultaneously or by steps. The authors proved that the protonization of the hydrogen atoms of C₄ is suppressed by the conjugation of the methyl group. Thus, the order of the mentioned cleavage reactions is predetermined according to scheme (I). ✓

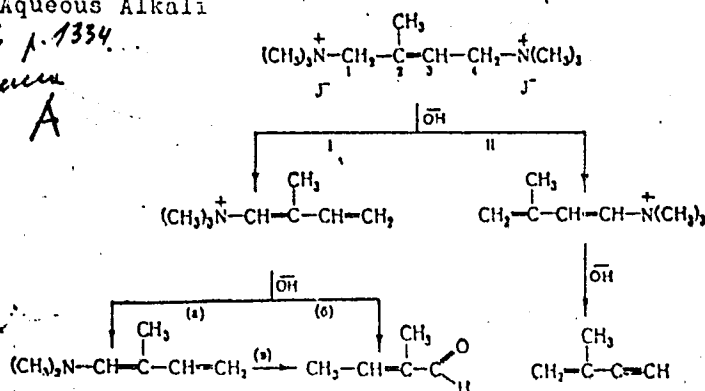
Card 1/6

Formation of Conjugate Diene Amines During the Interaction of Mono- and Diquaternary Salts of 1,4-Diamines With Aqueous Alkali

8133, 6 p. 1334.

Shen A

S/020/60/133/006/027/031XX
B016/B054



This statement by the authors is based on the results of their experiments. From the products of the reaction of the iodine salt of 1,4-di-(trimethylammonium)-2-methyl butene-2 with aqueous alkali, they isolated an aldehyde (corresponding to the dimer of methyl crotonic aldehyde), as well as a high-boiling amine product (apparently a condensation product of methyl crotonic aldehyde with 1-dimethyl-amino-(methyl)-butadiene). The same

Formation of Conjugate Diene Amines During
the Interaction of Mono- and Diquaternary
Salts of 1,4-Diamines With Aqueous Alkali

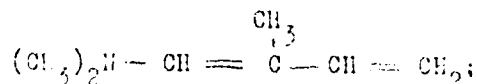
S/020/60/133/006/027/031XX
B016/B054

result was obtained in the transition from a mixture of quaternary ammonium salt with alkali to an ammonium base. The authors did not succeed (contrary to a statement made by Ya. M. Slobodin, Ref. 5) in detecting even traces of 2-methyl vinyl acetylene in the reaction products. This fact speaks in favor of scheme I. The authors further cleft the monoiodo methyl derivative of 1,4-di-(dimethyl-amino)-2-methyl butene-2 by aqueous alkali at a lower temperature (120°C). Here, the same products were formed as in the cleavage of the diquaternary salt. Subsequently, the authors cleft - in vacuo and at 105-107°C - the hydroxide they had produced by treating the monoiodo methylate of 1,4-di-(dimethyl-amino)-2-methyl butene-2 with an aqueous suspension of the silver oxide. Here, they isolated 1-dimethyl-amino-2-methyl butadiene-1,3 (yield about 70% of the theoretical one). The properties of this substance are described. From the fact that this substance forms dimethyl amine, as well as a corresponding derivative of α -methyl crotonic aldehyde, with the solutions of semicarbazide, 2,4-dinitro-phenyl hydrazine, and hydroxylamine, the authors conclude that the methyl in the diene amine takes a β -position with respect to the amino group:

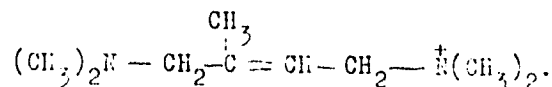
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Formation of Conjugate Diene Amines During
the interaction of Mono- and Diquaternary
Salts of 1,4-Diamines With Aqueous Alkali

S/020/00/133/006/027/031XX.
B016/P054



consequently, the position of the methyl in the monoiodo methylate used is:



On the basis of these results, the authors assume that the second cleavage step of diiodo methylate (step (a) of scheme I) requires a higher temperature (140-145°C) than was hitherto applied. To settle this question, they studied the behavior of two other diquaternary ammonium salts (I) and (II) towards aqueous alkali. It was proved that the alkaline cleavage of (I) already occurred at the temperature of the boiling water bath (see scheme B). The similar cleavage of (II) is illustrated by scheme C. Thus, the authors proved that the diquaternary ammonium salts (I) and (II) are cleft by alkali according to scheme I, i.e., exclusively via step (a) (see scheme A). There are 5 Soviet references.

Card 4/6

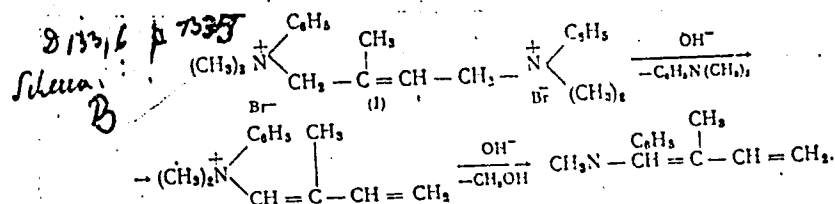
Formation of Conjugate Diene Amines During
the Interaction of Mono- and Diquaternary
Salts of 1,4-Diamines With Aqueous Alkali

S/020/60/133/006/027/031XX
B016/B054

ASSOCIATION: Institut organicheskoy khimii Akademii nauk ArmSSSR
(Institute of Organic Chemistry of the Academy of Sciences
Armyanskaya SSR)

PRESENTED: April 12, 1960, by I. L. Knunyants, Academician

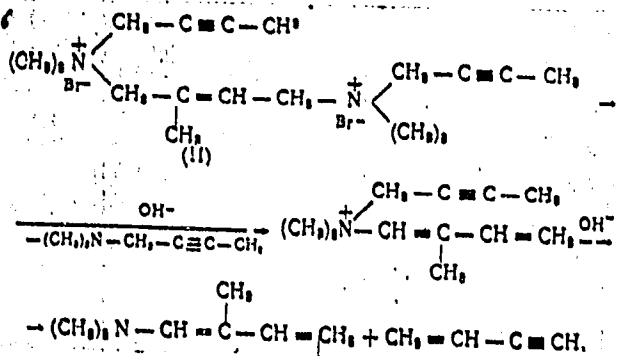
SUBMITTED: April 10, 1960



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S/020/60/133/006/027/031XX:
B016/B054

5,133-16 p. 1336
Scheme C.



✓

BABAYAN, A.T.; MARTIROSYAN, G.T.; VARTANYAN, N.G.; INDZHIKYAN, M.G.

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(MIRA 13:7)

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(MIRA 13:11)

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(Alkylation) (Ammonium salts)

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no.3:825-829 Mr '61. (MIRA 14:3)

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(Ammonium salts)

YEREVAN, A.S.

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PHASE I BOOK EXPLOITATION

30V/6195

Nauchnaya konferentsiya institutov khimii Akademiy nauk Azerbaydshanskoy, Armyanskoy i Gruzinskoy SSR. Yerevan, 1957.

Materialy nauchnoy konferentsii institutov khimii Akademiy nauk Azerbaydzhanskoy, Armyanskoy i Gruzinskoy SSR (Materials of the Scientific Conference of the Chemical Institutes of the Academies of Sciences of the Azerbaydzhian, Armenian, and Georgian SSR) Yerevan, Izd-vo AN Armyanskoy SSR, 1962. 396 p. 1100 copies printed.

Sponsoring Agency: Akademiya nauk Armyanskoy SSR. Institut organicheskoy khimii.

Resp. Ed.: L. Ye. Ter-Minasyan; Ed. of Publishing House: A. G. Silkuni; Tech. Ed.: G. S. Sarkisyan.

PURPOSE: This book is intended for chemists and chemical engineers, and may be useful to graduate students engaged in chemical research.

COVERAGE: The book contains the results of research in physical, inorganic, organic, and analytical chemistry, and in chemical engineering, presented at the Scientific Conference held in Yerevan, 20 through 23 November 1957. Three reports of particular interest are reviewed below. No personalities are mentioned. References accompany individual articles.

Materials of Scientific Conference (Cont.)	SOV/6195
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<u>Gogorishvili, P. V., and M. V. Karkarashvili.</u> Diamine Sulfite Complex Compounds of Divalent Cobalt	132
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<u>Zeynalov, B. K.</u> Oxidation of Paraffinic Distillate and Normal Hexadecane in the Presence of Chlorine and Nitrogen Dioxide	177

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BABAYAN, A. T.

JUN 25 1963

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PHASE I BOOK EXPLOITATION

SOV/6195

Nauchnaya konferentsiya institutov khimii Akademiy nauk Azerbaydzhanskoy, Armyanskoy i Gruzinskoy SSR. Yerevan, 1957.

Materialy nauchnoy konferentsii institutov khimii Akademiy nauk Azerbaydzhanskoy, Armyanskoy i Gruzinskoy SSR (Materials of the Scientific Conference of the Chemical Institutes of the Academies of Sciences of the Azerbaydzhan, Armenian, and Georgian SSR) Yerevan, Izd-vo AN Armyanskoy SSR, 1962. 396 p. 1100 copies printed.

Sponsoring Agency: Akademiya nauk Armyanskoy SSR. Institut organicheskoy khimii.

Resp. Ed.: L. Ye. Ter-Minasyan; Ed. of Publishing House: A. G. Silkuni; Tech. Ed.: G. S. Sarkisyan.

PURPOSE: This book is intended for chemists and chemical engineers, and may be useful to graduate students engaged in chemical research.

Card 1/11

Materials of the Scientific Conference (Cont.)

80V/6195

COVERAGE: The book contains the results of research in physical, inorganic, organic, and analytical chemistry, and in chemical engineering, presented at the Scientific Conference held in Yerevan, 20 through 23 November 1957. Three reports of particular interest are reviewed below. No personalities are mentioned. References accompany individual articles.

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- Nanobashvili, Ye. M., and L. V. Ivanitskaya. The Effect of γ -Radiation on Colloidal Solutions of Gallium, Indium, and Thallium Sulfide 23
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(Alkalies)

(Butynyl group)

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(PSYCHIATRY,

in Russia, develop. of psychiat. aid)

(NEUROLOGY,

in Russia, develop. of psychiat. aid)

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red. (Leningrad); LEBEDINSKIY, M.S., red. (Moskva); MYASISHCHEV,
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